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Theoretical Calculation of the Vibrational Spectra of Some XH_n Type Molecules

By

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The potential function of some molecules of type XH_n has been obtained by a priori calculations of the total energy, within the Born Oppenheimer approximation, for several geometrical configurations. These functions have been used to calculate the simply excited vibrational levels. The calculated values of the electric dipole moment for the different geometrical configurations has enabled the computation of its derivative with respect to the nuclear coordinates. The results reported are critically discussed and some explanations are presented to justify the discrepancies found with the experimental data.

La fonction potentiel de quelques molécules XH_n a été obtenue par le calcul a priori de l'énergie moléculaire, dans l'approximation de Born et Oppenheimer, pour plusieures configurations géométriques. Ces fonctions ont été utilisées pour calculer les vibrations monoexcitées. Les valeurs calculées du moment de dipole électrique pour différentes configurations donnent la possibilité de calculer ses dérivées par rapport aux coordonées nucléaires. On donne des justifications a l'accord peu satisfaisant entre les résultats et l'expérience.

Mittels einer apriorischen Berechnung der Gesamtenergie nach der Born-Oppenheimer-Methode ist die Potentialfunktion für einige Moleküle der Art XH_n in verschiedenen Konfigurationen erhalten worden. Diese Funktionen sind für die Berechnung der monoerregten Schwingungszustände gebraucht worden. Die berechneten Werte des elektrischen Dipolmoments für verschiedene Geometrien haben die Berechnung der Ableitungen des Dipolmoments nach den Kernkoordinaten erlaubt. Die erhaltenen Resultate werden diskutiert und einige Erklärungen vorgeführt, um die gefundenen Unterschiede von den experimentellen Ergebnissen zu klären.

I. Introduction

A priori calculation of vibrational spectra of molecules within the framework of the Born Oppenheimer approximation involves, among other things, the computation of the electronic molecular energies. This is certainly the most troublesome part of the calculation because it is not clear how the several approximations necessarily made at this stage will affect the final results. Naturally the effect of the other approximations is considered negligible in comparison, as it is well known and accurate calculations have shown [*12*].

The results which have appeared in the literature so far are not very extensive. Bishop et al. [*5*, *6*] considered some of the molecules we treated, by a method similar to ours, but only for a particular nuclear distortion, i. e. that of the "breathing" frequency which in general does not correspond to any normal mode.

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On the other hand BRATOZ et al. [*7*] treated a few molecules for all their vibrational modes but by a completely different and considerably simpler approach.

In our investigation the electronic energy for several nuclear arrangements was obtained by the OCE SCF MO method which was already described by one of us [*19*]. Therefore here we will give only a very brief description of it referring to those papers [*19, 20, 21*] for further details. In addition, the expectation value of the electric dipole moment was calculated also. These data were employed to evaluate, in a purely theoretical way, the vibrational spectrum of the following molecules:

$$HF, HCl, H_2O, H_2S, NH_3, PH_3, CH_4, SiH_4, NH_4^+, PH_4^+ .$$

For the NH_4^+ and PH_4^+ ions only the breathing vibration was considered which in these cases coincides with a normal mode.

II. Summary of the Method

To evaluate the expectation value of the electronic energy the wave function was approximated by a single detor of MO's each expressed as a linear combination of Slater type functions all centered upon the heavy nucleus. The coefficients of these linear combinations were determined by Roothaan SCF procedure. This method has been shown to be capable of giving satisfactory results for the XH_n type of molecules once enough basis functions are employed. As described in [*19*] the computations were carried out for several nuclear arrangements, which permitted the determination of the equilibrium configurations. A rather critical point concerns the choice of the orbital exponents ζ, which in principle should be different for each nuclear configuration. But, the optimization of the ζ's for each geometry being out of question because of the exceedingly great computer time needed, the ζ's were kept fixed and equal to those of the theoretical equilibrium configuration*.

Once the total energy being obtained for several sets of internal coordinates, it was an easy matter to derive an analytical expression for the potential energy. The most natural way is to use a power expansion around the minimum, or a point very close to it, as in fact has been done. The expansion points we have taken correspond to the lowest values of the energies which were obtained in the quoted investigations [*19, 20, 21*]. The power series, in terms of convenient sets of internal coordinates, which will be of the form

$$V\,(x_1, x_2, ..) = V^0\,(x_1^0, x_2^0, ..) + \sum_i K_i\,(x_i - x_i^0) + \tfrac{1}{2} \sum_{ij} K_{ij}\,(x_i - x_i^0)\,(x_j - x_j^0) + \,.. \tag{1}$$

has been truncated to the second order terms because of the low accuracy reached and the obvious advantages offerd to the subsequent calculations.

We have then employed a least squares procedure to obtain the best fit of the total energy values. The magnitude of the variations of the internal coordinates was such as not to exceed more than 50% the average displacement of the first vibrational excited states as calculated by experimental data.

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* All these computations were carried out with a 7090 IBM computer by one of us, R. MOCCIA, during his stay at the Laboratory of Molecular Structure and Spectra of the University of Chicago.

All coefficients have been included except for some particular cases where the calculations of the molecular energies were not performed for some geometrical arrangements necessary to obtain a complete system with respect to all the coefficients.

The potential function so obtained was used to calculate, by the Wilson's *F-G* method [*25*], the vibrational frequencies. The inverse kinetic energy matrix *G* was computed for the theoretical equilibrium configurations*.

To evaluate the derivative of the electric dipole moment with respect to the internal coordinates a graphic method was employed. In fact it was thought that a linear approximation would be enough and that little sense would be in the calculation of the electrical anharmonicity.

The potential functions obtained were used to calculate the interpolated points of the minima also. For all cases it was found that both the value of the energy and the geometrical configuration were practically identical to those already given.

III. Results

The molecules considered have been divided in four groups according to their symmetry. The internal coordinates are defined as variation of the bond lengths

Table 1

Molecule	Point Group	Rep.	Symmetry Coordinates
HF HCl	$C_{\infty v}$	Σ^+	$S = \Delta r$
H_2O H_2S	C_{2v}	A_1	$S_1 = 2^{-1/2} (\Delta r_1 + \Delta r_2)$ $S_2 = \Delta \alpha_{12}$
		B_2	$S_3 = 2^{-1/2} (\Delta r_1 - \Delta r_2)$
NH_3 PH_3	C_{3v}	A_1	$S_1 = 3^{-1/2} (\Delta r_1 + \Delta r_2 + \Delta r_3)$ $S_2 = 3^{-1/2} (\Delta \alpha_{12} + \Delta \alpha_{13} + \Delta \alpha_{23})$
		E	$S_{3x} = 2^{-1} (2\Delta r_1 - \Delta r_2 - \Delta r_3)$ $S_{3y} = 2^{-1/2} (\Delta r_2 - \Delta r_3)$ $S_{4x} = 2^{-1} (2\Delta \alpha_{23} - \Delta \alpha_{12} - \Delta \alpha_{13})$ $S_{4y} = 2^{-1/2} (\Delta \alpha_{13} - \Delta \alpha_{12})$
CH_4 SiH_4 NH_4^+ PH_4^+	T_d	A_1	$S_1 = 2^{-1} (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$
		E	$S_{2x} = 12^{-1/2} (2\Delta \alpha_{12} + 2\Delta \alpha_{34} - \Delta \alpha_{23} - \Delta \alpha_{24} - \Delta \alpha_{13} - \Delta \alpha_{14})$ $S_{2y} = 2^{-1} (\Delta \alpha_{13} - \Delta \alpha_{23} + \Delta_{24} - \Delta \alpha_{14})$
		F_2	$S_{3x} = 2^{-1} (\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4)$ $S_{3y} = 2^{-1} (\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$ $S_{3z} = 2^{-1} (\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$ $S_{4x} = 2^{-1/2} (\Delta \alpha_{23} - \Delta \alpha_{14})$ $S_{4y} = 2^{-1/2} (\Delta \alpha_{24} - \Delta \alpha_{13})$ $S_{4z} = 2^{-1/2} (\Delta \alpha_{34} - \Delta \alpha_{12})$

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* The least squares procedure and subsequent frequency calculation were carried out upon a Bendix G-20 electronic computer.

Table 2

	HF		HCl	
	Cal.	Exp.	Cal.	Exp.
r_e (a. u.)	1.730 (1.728)	1.733	2.406 (2.404)	2.409
ω (cm^{-1})	4518	4137 [*13*]	3446	2990 [*11*]
$(\delta\mu/\delta S)$ (D/Å)	3.15	±1.6 [*14*]	3.615	±0.95 [*23*]
K_{rr} (erg/cm^2)	$11.58 \cdot 10^5$		$6.857 \cdot 10^5$	

Table 3

	H_2O		H_2S	
	Cal.	Exp.	Cal.	Exp.
r_e (a. u.)	1.814 (1.814)	1.810	2.510 (2.509)	2.525
α_e	106.39° (106.54°)	105.05°	89.40° (89.36°)	89.40°
ω_1 (cm^{-1})	4411	3832 [*2*]	3112	2722 [*1*]
ω_2 (cm^{-1})	1364	1648 [*2*]	985	1215 [*1*]
ω_3 (cm^{-1})	4211	3943 [*2*]	2798	2733 [*1*]
$(\delta\mu/\delta S_1)$ (D/Å)	1.558	?	1.864	±0.044 [*10*]
$(\delta\mu/\delta S_2)$ (10^{-8}D/rd)	1.015	?	0.137	±0.075 [*10*]
$(\delta\mu/\delta S_3)$ (D/Å)	3.366	±1.3 [*3*]	2.033	?
K_{rr} (erg/cm^4)	$10.40 \cdot 10^5$		$5.219 \cdot 10^5$	
$K_{rr'}$ (erg/cm^2)	$0.246 \cdot 10^5$		$0.712 \cdot 10^5$	
$K_{\alpha\alpha}$ (erg/rd^2)	$0.477 \cdot 10^{-11}$		$0.498 \cdot 10^{-11}$	
$K_{r\alpha}$ (erg/rd · cm)	$0.351 \cdot 10^{-3}$		$-0.060 \cdot 10^{-3}$	

Table 4

	NH_3		PH_3	
	Cal.	Exp.	Calc.	Exp.
r_e (a. u.)	1.924 (1.928)	1.912	2.673 (2.672)	2.678
α_e	109.16° (108.90°)	106.80°	89.26° (89.80°)	93.17°
ω_1 (cm^{-1})	3672	3506 [*9*]	2839	2452 [*9*]
ω_2 (cm^{-1})	645	1022 [*9*]	902	1041 [*9*]
ω_3 (cm^{-1})	3874	3577 [*9*]	2791	2457 [*9*]
ω_4 (cm^{-1})	1035	1691 [*9*]	864	1154 [*9*]
$(\delta\mu/\delta S_2)$ (D/Å)	0.741	±0.396 [*16*]	0.771	±1.20 [*16*]
$(\delta\mu/\delta S_2)$ (10^{-8}D/rd)	−2.18	±1.53 [*16*]	0.420	±0.65 [*16*]
$(\delta\mu/\delta S_3)$ (D/Å)	2.25	±0.178 [*16*]	1.13	±0.80 [*16*]
$(\delta\mu/\delta S_4)$ (10^{-8}D/rd)	—	±0.344 [*16*]	—	±0.52 [*16*]
K_{rr} (erg/cm^2)	$8.152 \cdot 10^5$		$4.259 \cdot 10^5$	
$K_{rr'}$ (erg/cm^2)	$-0.0080 \cdot 10^5$		$0.0498 \cdot 10^5$	
$2\,K_{r\alpha} + K_{r\alpha'}$ (erg/cm · rd)	$-0.2083 \cdot 10^{-3}$		$0.0286 \cdot 10^{-3}$	
$K_{\alpha\alpha} + 2\,K_{\alpha\alpha'}$ (erg/rd^2)	$0.2511 \cdot 10^{-11}$		$0.446 \cdot 10^{-11}$	

Table 5

	CH_4		SiH_4		NH_4^+		PH_4^+	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
r_e (a. u.)	2.086 (2.080)	2.067	2.788 (2.787)	2.76	1.990 (1.990)	1.956	2.750 (2.750)	2.68
α_e	Tetr. (Tetr.)	Tetr.	Tetr. (Tetr.)	Tetr.	Tetr. (Tetr.)	Tetr.	Tetr. (Tetr.)	Tetr.
ω_1 (cm^{-1})	3709	3137 [9]	2542	2237 [17]	3634	3252 [15]	2462	?
ω_2 (cm^{-1})	1262	1567 [9]	845	974 [17]	—	?	—	?
ω_3 (cm^{-1})	3830	3158 [9]	2557	2312 [9]	—	?	—	?
ω_4 (cm^{-1})	1122	1357 [9]	714	940 [9]	—	?	—	?
$(\delta\mu/\delta S_3)$ (D/Å)	2.277	±0.833 [18]	0.713	?	—	?	—	?
$(\delta\mu/\delta S_4)$ (10^{-8}D/rd)	0.549	±0.373 [18]	0.852	?	—	?	—	?
K_{rr} (erg/cm²)	$7.866 \cdot 10^5$		$3.720 \cdot 10^5$		—		—	
$K_{rr'}$ (erg/cm²)	$0.0995 \cdot 10^5$		$0.0381 \cdot 10^5$		—		—	
$K_{rr} + 3\,K_{rr'}$ (erg/cm²)	$8.1645 \cdot 10^5$		$3.8343 \cdot 10^5$		$0.400 \cdot 10^5$		$0.231 \cdot 10^5$	
$K_{r\alpha} - K_{r\alpha'}$ (erg/cm·rd)	$0.0787 \cdot 10^{-3}$		$-0.0811 \cdot 10^{-3}$		—		—	
$K_{\alpha\alpha} - K_{\alpha\alpha''}$ (erg/rd²)	$0.3847 \cdot 10^{-11}$		$0.3095 \cdot 10^{-11}$		—		—	
$K_{\alpha\alpha'} - K_{\alpha\alpha''}$ (erg/rd²)	$0.0159 \cdot 10^{-11}$		$-0.0404 \cdot 10^{-11}$		—		—	

Δr and the bond angles $\Delta\alpha$ and they are conveniently combined to give symmetry coordinates whose definitions are reported in the following Tab. 1 together with their irreducible representation specifications.

The experimental quantities which we have chosen as comparison are the vibrational frequencies corrected for anharmonicity and the derivative of the total electronic dipole moment with respect to the symmetry coordinates. The harmonic frequencies have been chosen instead of the force constants because the latter are strongly dependent upon the particular force field employed and upon the inclusion or not of anharmonicity constants [*8*].

Anyway we report the force constants calculated together with the other data. In Tab. 2—5 all the results obtained are shown. The values of r_e and α_e given in parenthesis are those of the points of expansion. They are so close to the interpolated points of minima that the corresponding energy differences are of the order of magnitude of $10^{-5} - 10^{-6}$ a. u.

IV. Discussion

The results reported although qualitatively in fair agreement with the experimental data, quantitively are not very satisfactory. This can be taken as a clear indication that the vibrational frequency is a very critical property to be calculated and better wavefunctions are needed. But the amount of data we have obtained could permit us to draw some useful indication of the most evident faults of the wavefunctions for such a property, i.e. the rate of change of the molecular energy with the molecular displacements.

From an inspection of the results it is easy to perceive the general feature that the stretching modes are higher, the bending modes lower than the experimental values.

To interpretate this characteristic it is very convenient to use the idea of the force constant and, due to the low degree of approximation reached, of the diagonal term only. A suitable formula for the force constants can be derived by the use of the Hellmann and Feynman theorem [*24, 22*]. In this case we have

$$K_{xy} = \int \varrho \frac{\delta}{\delta x}\left(\frac{\delta V_{Ne}}{\delta y}\right) d\tau + \int \frac{\delta \varrho}{\delta x}\,\frac{\delta V_{Ne}}{\delta y}\, d\tau + \frac{\delta^2 V_{NN}}{\delta x\,\delta y} \qquad (2)$$

where V_{Ne} represents the total electron-nuclear attraction potential operator, V_{NN} the nuclear repulsion, x and y stand for any two internal coordinates, ϱ represents the first order spinless density matrix and the integration is carried on the spatial electronic variables. It must be understood that all these quantities are calculated at the equilibrium configuration. It is a simple matter, via perturbation theory, to show that Eq. (2) is symmetric in x and y [*22*].

Eq. (2) is suitable to a clear interpretation: the first and the last temrs represent the contribution to the force constant due to the electric charge distribution, both electronic and nuclear, considered fixed, while the second term, the relaxion term, is due to the polarization effect upon the electronic charge distribution. This term will always be such as to decrease the variation of energy due to the x and y variations. This means that its sign will be positive for a negative $x \cdot y$ product and viceversa. In particular it will be negative for the diagonal force constants. This is so because the charge redistribution will be such as to obtain an energetically stabler situation.

For the molecules here treated, the internal coordinates to be considered are the distance X–H for the stretching force constant and the angle H–X–H for the bending force constant. We wish to explain why the K_{rr}, the stretching force constants, are too large while the $K_{\alpha\alpha}$, the bending force constants, are too small. Here we will sketch the analysis which is carried out much more detailed in [*22*].

A first defect ascribable to the OCE MO SCF method in its limited form is the poor description of the charge distribution in the regions very close to the protons, far from expansion center, where it would be determined by a field of atomic character. Probably the situation is not very serious for the following reasons.

First of all we rewrite Eq. (2) as [*22*, *24*]:

$$K_{rr} = \int \varrho \, \frac{\delta^2 V_{Ne}}{\delta r^2} \, d\tau - \tfrac{4}{3} \pi \varrho (r_0) + \int \frac{\delta \varrho}{\delta r} \, \frac{\delta V_{Ne}}{\delta r} \, d\tau + \frac{\delta^2 V_{NN}}{\delta r^2} \qquad (3\,\mathrm{a})$$

$$K_{\alpha\alpha} = \int \varrho \, \frac{\delta^2 V_{Ne}}{\delta \alpha^2} \, d\tau - \tfrac{4}{3} \pi r_0^2 \varrho (r_0) + \int \frac{\delta \varrho}{\delta \alpha} \, \frac{\delta V_{Ne}}{\delta \alpha} \, d\tau + \frac{\delta^2 V_{NN}}{\delta \alpha^2} \, . \qquad (3\,\mathrm{b})$$

(3a) is for the stretching, (3b) for the bending force constants. The terms $-\frac{4}{3}\pi\varrho(r_0)$ and $-\frac{4}{3}\pi r_0^2 \varrho(r_0)$ are needed for the nuclei are considered point-like [*22*, *24*]. It is evident that the main error in ϱ is due to the charge $\delta\varrho_s$ which, being determined by the proton, will be spherically symmetric and will follow it rigidly.

This charge $\delta\varrho_s$ will have the correct behaviour in the region close to the proton and therefore will be responsable to satisfy the cusp conditions upon it [*4*]. But this correction $\delta\varrho_s$ will add nothing to (3a) and (3b) because:

1. $\frac{\delta^2 V_{Ne}}{\delta r^2}$ and $\frac{\delta^2 V_{Ne}}{\delta \alpha^2}$, with respect to a system of axis whose origin is located upon the proton, will have the expression of irregular spherical harmonics of degree two and a mixture of two and one respectively [*22*]. Not containing any spherical symmetric function they will give zero contribution with $\delta\varrho_s$ to the first integral terms of (3a) and (3b).

2. The contributions of $\delta\varrho_s$ to the second and third terms of (3a) and (3b) will compensate each other [*22*, *24*]. As a matter of fact this is a consequence of a more general theorem [*22*] which states that the contribution to the force constant of that part of ϱ (not necessarily spherical) which follows rigidly the moving nucleus will be zero when evaluated by Eq. (2).

Thus it seems reasonable to seek for other reasons to explain the systematic errors in K_{rr} and $K_{\alpha\alpha}$. To recognise the quite different situations for X_{rr} and $X_{\alpha\alpha}$ let us expand both the potential V_{Ne} and ϱ in series of spherical harmonics centered at X. After the integration over the angular variables is carried out, the double series arising in Eq. (2) will reduce to a single series (due to the orthogonality conditions). For the stretching force constant the series will start obviously with the monopole while for the bending one this term will necessarily be absent. This is so because the derivation with respect to angular variables of V_{Ne} will eliminate its monopole contribution. Thus the series for the bending force constants will start with the first multipole different from monopole compatible with the molecular symmetry [*22*]. Owing to the monopole contribution, which in our cases is the largest, the expectation value of the field gradient due to the electrons [the first term of Eq. (2)] for K_{rr} must be large and negative while for $K_{\alpha\alpha}$ it must be much smaller in absolute value and positive [*22*]. If ϱ is badly represented around the protons having a smoother behaviour than what should be, the expectation value of the field gradient will be smaller in absolute value giving errors of different signs upon the force constants. To this must be added the error upon the relaxation term which will be more serious for the stretching motions than for the bending ones, because ϱ, deriving from a limited one center expansion with fixed basis functions, will certainly be polarized more easily along the bending motions than along the stretching ones.

It is understandable therefore why the stretching force constants are higher while the bending ones are lower than the experimental values. These considerations indicate that the force constants are quantities difficult to calculate because, unless there is a fortunate compensation of errors [*10*], we have to reproduce accurately both the charge distribution and its variations with the internal coordinates. While the first of these quantities can be approximated rather reliably by a best single detor wavefunctions i.e. by Hartree and Fock wavefunctions, the second is much more delicate to evaluate.

This situation can be recognised if we remember that the best single electronic configuration should be changed when varying the internal coordinates [*21*]. In our opinion this effect will be much more pronounced for the stretching motion than for the bending one. Thus increasing the size of the basis set of the OCE SCF MO method we expect to improve the results more for the bending than for the stretching force constants. These will still remain too large. The same effect is encountered for the derivatives of the electric dipole moments, where it is quite clear, form their too large values, that the low flexibility of ϱ is the main cause for it.

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